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LUMINESCENCE CHARACTERISTICS OF ALKALI BORATE GLASSES

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Pulsed cathodoluminescence was used to study the luminescence of alkali borate glasses of the systems $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$ and $\text{Na}_2\text{O} - \text{B}_2\text{O}_3$. The results are compared with a study of the anionic structure of these glasses. It is established that the intensity of the cathodoluminescence increases with increasing fraction of alkali metals in the glasses; it is determined by the fractions of the nonbridge bonds $\text{M} - \text{O} - \text{B}$ – in the structure of these glasses and differs in lithium and sodium glasses.

Key words: cathodoluminescence, borate glasses, structure.

Borate glasses are an important class of oxide glasses, whose anionic structure consists of diverse structural and superstructural units represented by different boro-oxygen groupings and complicated anionic complexes [1, 2]. It has been determined that when the framework of alkali borate glasses undergoes polymerization bridge bonds of the type $-\text{B} - \text{O} - \text{B}-$ as well as nonbridge bonds $\text{M} - \text{O} - \text{B}-$ coordinated by alkali metal ions ($\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}, \text{Li}$) can form. The fraction of the nonbridge bonds is related with the ratio of boron in ternary and quaternary coordination, depends on the alkali-metal fraction, and has a large effect on the physical properties of glass [3, 4]. Increasing the alkali-metal content in the glass composition does not always increase the fraction of nonbridge bonds [5]; this is why it is important to determine the number of nonbridge bonds correctly. Vibrational spectroscopy, such as infrared spectroscopy and Raman scattering spectroscopy, cannot solve this problem. This is due to the complexity of the decomposition of the spectra, the impossibility of clearly distinguishing in them bands which are related with the vibrations of nonbridge bonds, as well as a considerable error in calculating from the intensity of these bands the nonbridge-bond fraction [6].

The luminescence of glass, as other dielectric materials and substances, is determined by impurities and structural defects of different kinds as well as the formation of centers of luminescence of different nature [7]. Recently, pulsed cathodoluminescence (PCL) has been widely used to study the luminescence properties of glasses [8 – 9]. The high information content and the effectiveness of this method are

due to the use of pulsed excitation and to the short-time local supercooling of the sample under the action of a high-current electron beam [10]. The manifestation of the cathodoluminescence of alkali silicate glass was described in [9 – 11], and the mechanism was tied to the formation of nonbridge oxygen atoms in the glass structure. This indicates the possibility of using the PCL method to study the structural features of other types of oxide glasses. The authors of the present article assumed that there should be a correlation between the intensity of the cathodoluminescence of alkali borate glasses and the fraction of nonbridge oxygen (NBO) atoms in their structure.

The luminescence characteristics of alkali borate glasses were studied by means of pulsed cathodoluminescence of a series of lithium and sodium borates glasses with different alkali-metal fraction.

To determine the luminescence properties of lithium and sodium borate glass, glass with the following composition was synthesized: $x\text{Li}_2\text{O} + (1 - x)\text{B}_2\text{O}_3$ and $x\text{Na}_2\text{O} + (1 - x)\text{B}_2\text{O}_3$, where $x = 5, 30, 40$, and 50 is the molar fraction of the components. The glass was synthesized by melting prepared mixes of chemically pure reagents Li_2CO_3 , Na_2CO_3 , B_2O_3 , and SiO_2 in platinum crucibles at 1200°C followed by rapid cooling (quenching). For this the melt was poured into a special disk-shaped recess on a metal plate.

The pulsed cathodoluminescence (PCL) spectra were recorded using a KLAVI-R cathodoluminescence pulsed analyzer of materials, developed at the Institute of Electrophysics at the Urals Branch of the Russian Academy of Sciences. A sample holder with the same recess as in the mold used to quench the samples was made to record the spectra of the glasses obtained. The glasses were irradiated by a packet of 32 1-nsec pulses with repetition frequency 1 Hz. The PCL

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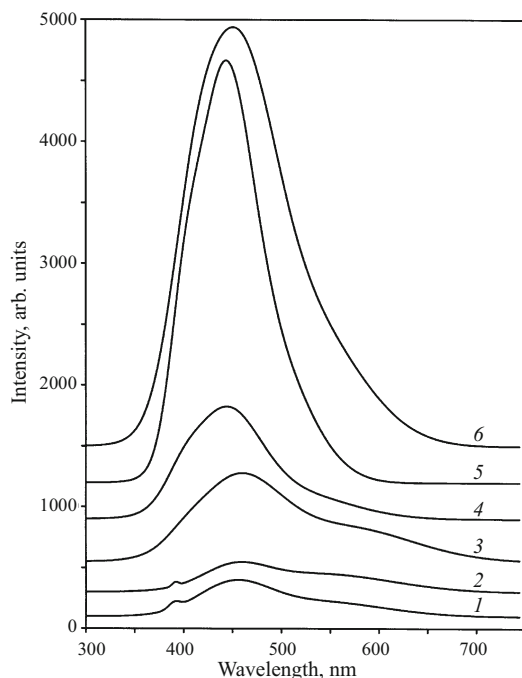


Fig. 1. PCL spectra of synthesized glasses after smoothing: 1) $5\text{Na}_2\text{O} - 95\text{B}_2\text{O}_3$; 2) $5\text{Li}_2\text{O} - 95\text{B}_2\text{O}_3$; 3) $30\text{Na}_2\text{O} - 70\text{B}_2\text{O}_3$; 4) $30\text{Li}_2\text{O} - 70\text{B}_2\text{O}_3$; 5) $40\text{Na}_2\text{O} - 60\text{B}_2\text{O}_3$; 6) $50\text{Li}_2\text{O} - 50\text{B}_2\text{O}_3$.

spectra were recorded in the optical wavelength range (390 – 800 nm).

The PCL spectra of all experimental borate glasses are characterized by the presence, at the center of the recorded range, of an asymmetric band with maximum near 445 – 450 nm (Fig. 1). As the metal-oxide content of the glass increases, the intensity of this band in the spectra of the glasses of both series increases. Its intensity in the spectra of the glasses in the sodium system as compared with the spectra of glasses in the lithium system is higher and the maximum is displaced into the long-wavelength part of the spectrum.

The decomposition of the spectra obtained into Gaussian lines showed that the luminescence band observed in the PCL spectra can be represented by a superposition of three components (Fig. 2). The low-frequency component is a narrow line with a maximum near 395 – 405 nm. The line with a maximum near 440 – 450 nm makes the main contribution to the luminescence band. The high-frequency component is represented by a band peaking at 500 nm with a shoulder near 560 nm. In lithium series glass this shoulder has a much higher intensity than in the sodium system. As the alkali-metal fraction increases, the main change of the intensity of the luminescence of the glass is due to an increase of the intensity only of the central component of the band.

Comparing the data on the anionic structure of borate glasses obtained by other methods [12] showed that this change in the intensity is correlated with a change in the fraction of nonbridge bonds $\text{M} - \text{O} - \text{B}$ in the structure of these glasses. It was shown that if the alkali-metal content is low,

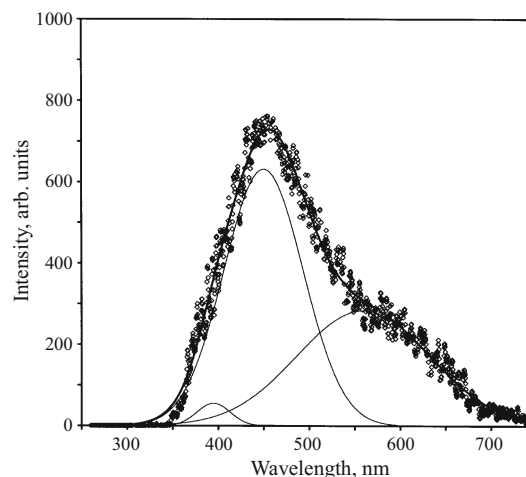


Fig. 2. Smoothing-decomposition procedure for PCL spectra (exemplified in $30\text{Li}_2\text{O} - 70\text{B}_2\text{O}_3$ glass).

then nonbridge bonds are unlikely to form. This is reflected in the low intensity of the PCL spectra of glasses with the compositions $05\text{Li}_2\text{O} - 95\text{B}_2\text{O}_3$ and $05\text{Na}_2\text{O} - 95\text{B}_2\text{O}_3$, which is due to the existence of luminescence centers of a different kind. Increasing the alkali-metal content gives rise to breaking of the bridge bonds $\text{B} - \text{O} - \text{B}$ and the alkali-metal ions act as coordinators of the charge of the nonbridge oxygen atoms. This corresponds to an increase of the intensity of the bands in the PCL spectra of glasses with the compositions $30\text{Li}_2\text{O} - 70\text{B}_2\text{O}_3$ and $30\text{Na}_2\text{O} - 70\text{B}_2\text{O}_3$. According to NMR data [12] and the Krogh – Moe model [13], an appreciable content of nonbridge bonds should be observed with alkali-metal fraction of about 30 – 35%, which determines the maximum intensity of the luminescence in the PCL spectra of samples of glasses with the composition $40\text{Na}_2\text{O} - 60\text{B}_2\text{O}_3$ and $50\text{Li}_2\text{O} - 50\text{B}_2\text{O}_3$.

The results of the analysis of the PCL spectra of the synthesized glasses show that every nonbridge oxygen atom in the structure of alkali borate glass can indeed appear with high probability as an ion-luminogen and participate in the formation of a luminescence center. The observed difference in the intensity and shape of the dominant band in the spectra of the sodium and lithium glasses shows that they have different effects on the formation of nonbridge bonds $\text{M} - \text{O} - \text{B}$ in the structure of borate glasses, which is probably due to the difference of the ionic radii of the lithium and sodium.

CONCLUSIONS

The following conclusions can be drawn from the results of this investigation:

intense cathodoluminescence is characteristic for sodium and lithium borate glasses;

the intensity of the cathodoluminescence of these glasses depends on the alkali-metal content in the composition of the glass;

the centers of the observed cathodoluminescence are related with the nonbridge oxygen atoms in the composition of the bonds $M-O-B$ in the structure of these glasses;

the intensity of the luminescence in the sodium-borate glasses is higher than in sodium glasses, which indicates that these ions have a difference effect on the formation of the nonbridge bonds in the structure of alkali borate glasses.

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